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(54) **Water-reducible dye compositions.**

(57) Water-immiscible dyes are mixed with citrus solvents and non-ionic surfactants to form a water-reducible true dye solution containing at least 35 wt% of the water-immiscible dye. The dye solution is dispersible in water and infinitely reducible.

The present invention is directed to water-reducible dye compositions which, upon mixing with water, form aqueous dispersions of the dyes and to the aqueous dispersions formed therefrom.

There are a wide variety of types of dyes which are water-immiscible. A major advantage of water-immiscible dyes is that such dyes tend to be permanent, at least with respect to exposure to water. A disadvantage of such dyes is that they require organic solvent carriers, such as xylene, which are problematic from a health and environmental standpoint.

The present invention is directed to compositions of water-immiscible dyes which form stable dispersions in aqueous media and therefor provide the permanence of water-immiscible dyes without the accompanying disadvantage of containing harmful organic solvent carriers.

For many industrial applications, such as for forming inks, high dye loadings are required. Dye solutions typically must be formulated with a variety of additional ingredients which dilute the coloring effect of the dye; hence, the need for high dye loading. Furthermore, the solvent used to dissolve the dye may not be desirably used at a high level in the formulation. Accordingly, it is a further object of the invention that the water-reducible dye solutions have high dye loadings.

Water-reducible dye solutions of the present invention comprise between about 35 wt% and about 70 wt% of a) a water-immiscible dye selected from the dye types consisting of azo type dyes, phthalocyanine type dyes, and anthraquinones; between about 10 and about 64 wt% of b) a solvent system for said water-immiscible dye in sufficient quantities to dissolve said water-immiscible dye, said solvent system comprising between about 30 and about 100 wt% of b1) a citrus solvent(s) and b2) between 0 and about 70 wt% of a compatible co-solvent(s) which is either water-miscible or water-immiscible; and c) between about 1 and about 55 wt% of a non-ionic surfactant. When mixed into water, the water-reducible solutions form stable micro dispersions of the water-immiscible dye solutions in the water, which dispersions are infinitely reducible. The dyes of such aqueous dispersions become permanently fixed to the material to which they are applied.

Water-immiscible dyes to which the present invention applies are:

1. Azo types which includes monoazo, disazo and tetrazo's of both the metallized and non-metallized varieties. Metallized dyes are typically described as amine salts of monatomic metal chelates with one or two molecules of dye, depending upon the metal used. Non-metallized azo dyes include guanidine salt types typical of the Luxol^R product line. Specific examples of water-immiscible azo dyes include but are not limited to are:

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1- Automate[®] Black 104 = c.i. Solvent Black 49 = benzene azobenzene naphthyl benzeneamino hydroxy, alkyl derivatives/alkylamino-cuprate. CAS Accession # 56918.

2- Automate[®] Yellow D - c.i. Solvent Yellow, 4 - (2-hydroxy-5-nonylphenylazo) - [N-[4- (2-hydroxy-5-nonylphenylazo) - phenyl]] benzamide. CAS # PMN Notice No. P-91-890.

3- Automate[®] Red B = c.i. Solvent Red 164 = 2-naphthalenol (phenylazo) phenyl azo alkyl derivatives. CAS # = TSCA accession # 35371.

4- Morfast[®] Red 101 = c.i. Solvent Red 68 = 1,3-naphthalenedisulfonic acid, 7-hydroxy-8-4- (phenyl-azo) phenyl azo-, compound with 2-ethyl-N-(2-ethylhexyl)-1-hexanamine (1:2). CAS # = 68555-82-8.

5- Morfast[®] Black 101 = c.i. Solvent Black 48 = cobaltate bis-2, 2'-dioxy-4-di 2"-hydroxy-3"-alkoxypropyl amino-4-phenylazo-5-methylazobenzene, hydrogen dibutanammonium salt.

6- Luxol[®] Brown K = c.i. Solvent Brown 20 = 1,3-naphthalenedisulfonic acid, 7,7' (4,6-dihydroxy -1,3-phenylene) bis (azo) bis arylguanidine salt. CAS # 72208-28-7.

7- Automate[®] Yellow 126 - c.i. Solvent Yellow = 1,3 benzenediol, 2,4-bis (alkyl phenyl) azo-. CAS # 29190-28-1; 65087-00-5; and 68310-04-3.

2. Phthalocyanine derived dyes, mainly of the sulfonated versions derived from copper pigments. Specific examples include but are not limited to:

1- Morfast[®] Blue 100 = c.i. Solvent Blue 129 = cuprate (2-), 29H, 31H phthalocyanine disulfonato (4-) N29, N30, N31, N32 di-1-alkanammonium, -N-(alkyl) salt CAS # 68155-92-0.

2- Luxol[®] Blue MBSN = c.i. Solvent Blue 38 = cuprate (2-), 29H, 31H-phthalocyanine-disulfonato (4)-N29, N30, N31, N32-arylguanidine salt. CAS # 1328-51-4.

3. Anthraquinones, predominantly, mono, di and mixed substituted alkylamino derivatives as well as mono, di and mixed substituted arylamino types. Specific examples include but are not limited to:

1- Automate[®] Blue 8 = c.i. Solvent Blue 98 = 1,4-dialkylamino anthraquinone. CAS # 74499-36-8.

2- Automate[®] Green 5 = c.i. Solvent Green = 9,10-anthracenedione, 1,4-bis [(alkylphenyl) amino] anthraquinone. CAS #: none assigned.

3- BASF's Flussig Blue 672 = c.i. Solvent Blue 79 1,4-dialkoxyamino anthraquinone.

The term "Citrus Solvent" is used herein inclusively to include chemicals defined as citrus peel oils, terpene, terpinene, and dipentene. The definitions of

these classes in Hawley's Condensed Chemical Dictionary, Eleventh Edition overlap:

"Citrus Peel Oils" - Edible oils expressed from the peel or rind of grapefruit, lemon, lime, orange and tangerine; Constituents: limonene, citral, and terpenes in varying percentages.

"Terpene" - $C_{10}H_{16}$ An unsaturated hydrocarbon occurring in most essential oils and oleoresins of plants. The terpenes are based on the isoprene unit C_5H_8 , and may be either acyclic or cyclic with one or more benzenoid groups. There are classified as monocyclic (dipentene), dicyclic (pinene) or acyclic Myrcene, according to the molecular structure.

"Terpinene" - $C_{10}H_{16}$ A mixture of three isomeric cyclic terpenes, alpha, beta and gamma terpinene.

"Dipentene" - (cinene; limonene, inactive; dl-p-mentha-1,8-diene; cajputene); Commercial form is high in dipentene content, but also contains other terpenes and related compounds in varying amounts.

"Limonene" - a widely distributed optically active terpene, closely related to isoprene. It occurs naturally in both D- and L- forms. The racemic mixture of two isomers is known as dipentene.

Citrus solvents are found to be particularly useful solvents in providing dispersions of a wide variety of dyes. In addition, citrus solvents are non-toxic, environmentally safe and biodegradable. The citrus solvent may comprise 100% of the solvent of the water-reducible dye composition, or may be admixed with [up to about 70% by weight of] a co-solvent up to a 30/70 citrus solvent/co-solvent wt. ratio, preferably one which is likewise non-toxic and environmentally benign. Examples of suitable co-solvents include but are not limited to ethyl lactate, butyl lactate, propylene glycol, triethanolamine, methyl ethyl ketone, ethanol, methanol, diethanolamine, methyl lactate, xylene, 1-methoxy-2-propanol, 2-methoxy-1-propanol.

The third essential component is a non-ionic surfactant. Suitable surfactants include fatty acid esters; polyoxyethylated nonyl phenol derivatives; Rhone Poulenc - CO-720 and CO630 nonylphenoxypoly (ethyleneoxy) ethanol CAS # 9016-45-9; Union Carbide - Tergitol D-683 alkoxylated alkylphenol CAS # 37251-69-7; Rhone Poulenc - Alkamide 2106 modified coconut diethanolamide CAS # 68603-42-9; Rhone Poulenc - Alkamuls EL-985 polyethoxylated castor oil CAS # 75-21-8; and Morton International - Sotex N long chain fatty acid esters.

The specific dye types discussed above can be loaded in citrus solvent compositions to high levels, i.e., at least about 35 wt% and some up to about 70 wt%. This high loading is unexpected. U.S. Patent No. 5,092,907 describes dispersions of pigments in terpene oil. It also suggests that soluble dyes may be dissolved in terpene oil, but to a maximum of 30%. Thus that it is found that loading levels of 35 wt% or greater of particular dye types in citrus solvents can be achieved is unexpected. As stated above, high dye

levels are advantageous in that the industry requires high dye loadings, particularly for dye compositions which will be subsequently diluted by other components of particular formulations.

These components a) - c) are blended together to form a stable water-reducible true dye solution in accordance with the present invention. The dye solution is typically provided free of water for shipment and storage. The end user adds the dye solution to water (or aqueous medium) with appropriate agitation to produce a dispersion of the dye solution in water (or aqueous medium). Generally, stable dispersions are achieved at a 1:1 ratio of water reducible dye dye solution to water. However, the dye solution can accommodate more or less water, so as to provide the dye content the user desires.

Aqueous dispersions of the dye solution of the present invention can be used for example in felt tip pens, ball point pens, printing inks, hand stamps, ink jet inks, coatings, paints and woodstains.

The invention will now be described in greater detail by way of specific examples.

Example 1

To a 1 liter round bottom flask was charged 200 grams of a xylene solution of benzene azobenzene naphthyl benzeneaminohydroxy, alkyl derivatives/alkylaminocuprate. The dye was heated to 120°C under full vacuum to distil out all xylene (approximately 48%). The xylene is replaced with 90 grams ATR-High Flash^R citrus solvent and 10 grams long chain fatty acid ester.

This solution when mixed with 204 ml. water with stirring formed a dispersion of the dye solution.

Example 2

A water-dispersible solution was prepared in the manner of Example 1 containing 40 wt% 4-(2-hydroxy-5-nonylphenylazo)-[N[4-(2-hydroxy-5-nonylphenylazo)-phenyl]] benzamide, 36 wt% ATR-P citrus solvent and 24 wt% Igepal^R CO630.

Example 3

A water-dispersible solution was prepared in the manner of example 1 containing 35 wt% 1,4 dialkylamino anthraquinone, 46 wt% Vortex^R citrus solvent and 19 wt% long chain fatty acid ester.

Example 4

A water-dispersible solution was prepared in the manner of Example 1 containing 40 wt% cuprate (2-), 29H, 31H phthalocyanine disulfonate (4-) N29, N30, N31, N32 di-1-alkanammonium, -N-(alkyl) salt, 20 wt% butyl lactate, 20 wt% Vortex^R citrus solvent, 5

wt% long chain fatty acid ester, 10 wt% triethanol amine, and 5 wt% Pegospherse^R dispersing agent.

Example 5

A water-dispersible solution was prepared in the manner of Example 1 containing 46 wt% cobaltate bis-2,2"-dioxy-4-di 2"-hydroxy-3"-alkyloxy-propyl amino-4-phenylazo-5-methyl-azobenzene, hydrogen dibutanammonium salt, 40 wt% dipentene and 14 wt% long chain fatty acid ester.

Commercial citrus solvent/surfactant compositions useful in the present invention are analyzed as follows:

ATR-C: The major component appears to be limonene. The surfactant was identified as a mixture of ethoxylated alkyl phenols with the average structure $C_{12.7}H_{26.4-p}C_6H_4-O-(CH_2CH_2-O)_7H$. Assuming an average molecular weight of 580, the surfactant was estimated to be approximately 7 wt% of the sample.

Vortex: This sample appears to be very similar to ATR-C. The major component is limonene; the surfactant appears to be a mixture of ethoxylated alkyl phenols.

ATR-HI FLASH: The major component is terpinolene. The surfactant was identified as an ethoxylated alkyl phenol with an average surface structure $C_{17.7}H_{36.8-p}C_6H_4-O-(CH_2CH_2-O)_{5.3}H$.

IGEPAL 630: this sample was a surfactant that was known to be an ethoxylated alkyl phenol. NMR spectra determined an average structure $C_{8.7}H_{18.5-p}C_6H_4-O-(CH_2CH_2-O)_{8.6}H$.

ATR-P: The NMR spectra of this sample are very complex. The terpenoid component is a complex mixture, containing limonene as well as many other components. An ethoxylated surfactant appears to be present at a higher level in this sample. The ethoxylated segments appear to contain some oxymethylene groups. The surfactant may be an ethoxylated alkyl phenol, but due to the complexity of the spectra and the diversity in the structures, positive identification is very difficult. A small carbonyl component, possibly an ester, was also detected in this sample.

Dipentene: This sample also appears to be quite complex. The terpenoid solvent contains limonene as well as a number of other components. Its distribution is somewhat similar to that of ATR-P. The surfactant in this sample is similar to that of ATR-P. No carbonyl component was detected.

Claims

1. A water dispersible composition comprising between 35 wt% and 70 wt% of a) a water immiscible dye selected from the dye types consisting of azo type dyes, phthalocyanine type dyes, and anthraquinones;

between 10 and 64 wt% of b) a solvent system for said water-immiscible dye in sufficient quantities to dissolve said water-immiscible dye, said solvent system comprising

between 30 and 100 wt% of b1) a citrus solvent(s) and

b2) between 0 and 70 wt% of a compatible co-solvent(s) which is either water-miscible or water-immiscible; and

c) between 1 and 55 wt% of a non-ionic surfactant.

2. The composition of claim 1 dispersed in an aqueous medium.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 2233

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
P,X	WO-A-93 17166 (ARROW ENGINEERING, INC.) * page 8, line 6 - line 7 * ---	1,2	C09B67/44
A	EP-A-0 390 729 (SICPA HOLDING S.A.) * abstract * * page 4, line 34 - line 36 * D & US-A-5 092 907 (...) ---	1,2	
D			
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 122 (C-488)(2969) 15 April 1988 & JP-A-62 244 370 (SANEI CHEM. IND. LTD.) 24 October 1987 * abstract * -----		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C09B
Place of search	Date of completion of the search	Examiner	
THE HAGUE	12 July 1994	Ketterer, M	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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